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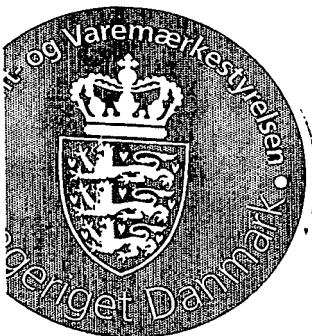
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Patent- og Varemærkestyrelsen
Økonomi- og Erhvervsministeriet

28 July 2004

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PATENT- OG VAREMÆRKESTYRELSEN

A METHOD OF PRODUCING AN INTERPENETRATING POLYMER NETWORK (IPN), THE IPN AND USE THEREOF

5 TECHNICAL FIELD

10 The present invention relates to a method of producing an interpenetrating polymer network (IPN) and an IPN obtainable according to the method as well as applications of such IPN.

BACKGROUND ART

15 IPNs have been known for more than 40 years. IPNs are defined as macromolecular assemblies comprising two or more polymers wherein at one is in the form of a network, the polymers are at least partially interlaced on a molecular scale but not covalently bonded to each other.

20 Because there is no chemical bonding between the networks (or polymer/network), each network may retain its individual properties independently of its individual proportion in the blend. As a result an improvement can be attained in properties such as mechanical strength, impact resistance, and toughness and other. There are two main types of IPNs, viz semi-IPN where at least one component are not in network form, 25 and full IPN where all species are in network form.

30 US 2002/01222946 relates to a process of producing an IPN comprising: providing a liquid mixture comprising silicone oligomers and silsesquioxane oligomers; and curing the liquid mixture to form a composition of first and second polymers, the first polymer comprising the silsesquioxane oligomers cross-linked by siloxane bonds and the second polymer comprising a cross-linked silicone network formed in part from the silicone oligomers.

35 US 20030000028 provides a colorant for use in tinting contact lenses in which the binding polymer used is capable of forming an interpenetrating polymer network with the lens material. When the colorants of the invention

are applied to uncured lens material that is subsequently cured, the binding polymer forms an interpenetrating polymer network with the lens material embedding the colorant within the lens material resulting in a stable, tinted lens.

5

Several other methods for producing IPNs are known. The methods e.g. includes simultaneously forming and crosslinking the polymer networks in the presence of each other. Other methods includes forming a first network and thereafter swelling this network with monomers, crosslinking agents and optionally initiator/catalyst with or without solvents where after this monomer may form a polymer and optionally a network, e.g. as disclosed in US 2002/0052448.

10
15

Prior art silicone IPN's are made by vulcanizing or crosslinking block copolymers, such as adducts of silicone molecules and other polymer blocks, such as ethers, urethanes, and the like. However, using prior art methods, the types of silicone IPNs and the freedom of design of properties of the IPNs are very limited.

20

Even though there are a lot of well working method for producing IPNs there is still needs for new alternative methods in particular for producing silicone IPNs.

SUMMARY OF INVENTION

25

The objective of the present invention is to provide an alternative or an improved method of producing an IPN, which method is simple to use and inexpensive, and whereby a full IPN can be obtained.

30

Furthermore it is an objective to provide a method of producing an IPNs which method also can be used for the production of IPNs which are complicated or impossible to produce using the prior art methods.

This and other objectives as disclosed in the following description have been achieved by the invention as it is defined in the claims and described in the description.

- 5 The inventor has thus found that by using a solvent with low surface tension for monomers to be precipitated within a silicone polymer composition, it is very fast to load monomers into the silicone polymer composition and furthermore it is possible to load monomers which not previously have been possible to load into silicone polymer compositions.

10

Further more the amount of monomers that can be loaded into the silicone polymer composition may be relatively high compared to when using prior art methods.

15 DISCLOSURE OF INVENTION

The method according to the invention of producing an interpenetrating polymer network (IPN) comprises the following steps:

- 20 i) providing a silicone polymer composition,

ii) providing one or more monomers for a polymer,

iii) providing a solvent for the one or more monomers,

25

iv) exposing said silicone polymer composition to said one or more monomer and said solvent to precipitate monomer within said silicone polymer composition

- 30 v) polymerizing said monomer to form an IPN.

The silicone polymer composition may in principle be any type of silicone polymer composition, but basically the best result is obtained if the silicone polymer composition comprises at least 10 %, such as at least 20%, such as

at least 40%, such as at least 60 % by weight of polymer having a backbone consisting of Si and O molecules.

5 In one embodiment the silicone polymer composition comprises at least 10 %, such as at least 20%, such as at least 40%, such as at least 60 % by weight of polymer having a backbone consisting of Si molecules.

10 In one embodiment the silicone polymer composition comprises at least 10 %, such as at least 20%, such as at least 40%, such as at least 60 % by weight of polysiloxane polymer.

15 Examples of useful silicones which separately or jointly can be comprised in the silicone polymer composition are dimethyl polysiloxan, methylphenyl polysiloxane, fluorosilicone rubber, silicone esters, polysiloxanes, polysilanes, chlorosilanes, alkoxysilanes, aminosilanes, polysilanes polydialkylsiloxanes, polysiloxanes containing phenyl substituents, said polymers of the silicone polymer composition optionally being vinyl-functionalized and/or optionally being partially or fully fluorinated.

20 The remaining of the silicone polymer composition may include other polymer, fillers and additives.

25 In one embodiment the silicone polymer composition comprises up to 90 % by weight of non-silicone polymers or co-polymers, fillers and/or additives.

30 The non-silicone polymers may e.g. be thermoplastics or thermosets, preferably selected from the group consisting of polyolefins, polyesters, polyurethanes, polycarbonates, polyvinyl polymers. In one embodiment the non-silicone polymers are selected from the group of polyamide, polyesters, polyether, polyethylene glycol, polysaccharide, cellulose, polyethylene, polypropylene, polybutylene, polyacrylonitrile, polyurethane, poly(vinyl chloride), poly(methyl methacrylate), polystyrene, polysulfone, polycarbonate, fluoropolymers such as polytetrafluoroethylene, polyvinylidifluoride, synthetic and natural rubber, thermoplastic elastomer,

phenol-formaldehyde, melamine-formaldehyde, and urea-formaldehyde,-and mixtures thereof.

- 5 The fillers may e.g. be particles or fibres e.g. in the form of minerals or organic fillers, preferably selected from the group consisting of silica, metals, metal oxides, mixed metal oxides, glass beads or glass fibers. Other examples of fillers are those that are disclosed in US 5,968,652, US 2001/00366617, US 5,861,445 and US 4,740,538, and in the co pending application filed simultaneously with this application by the same applicant.
- 10 The additives may e.g. be selected from the group consisting of adhesion promoters for 2K-constructions, process and plasticizing oils, antioxidants and pigments.
- 15 The silicone polymer composition may be partly or totally vulcanized. The vulcanization degree has influence on its swelling properties, and consequently a totally vulcanized silicone polymer composition may for some compositions be difficult to swell with the solvent carrying large monomers.
- 20 The silicone polymer composition may also deliberately be only partly vulcanized, such as below 98%, such as below 95%, in order to enlarge the "channels" or cavities in which reactive monomers are deposited.
- 25 In one embodiment the silicone polymer composition is partially vulcanized, such as up to a vulcanization degree (cross-linking degree) of at least 50%, such as at least 70%, such as at least 90% or wholly, such as at least 96%, such as at least 97%, such as at least 98%.
- 30 In one embodiment the silicone polymer composition is a vulcanized rubber.
- 35 The silicone polymer composition may preferably be at least partly transparent. In one embodiment a transparent silicone polymer composition is loaded with monomer and e.g. peroxides and is thereafter subjected to an activation step e.g. heating for polymerization and crosslinking the monomers. The resulting product is of milky-white appearance, presumably

due to a microstructure of small domains in size below or in the order of the wavelength of visible light, in addition due to different refractive indices of silicone versus monomer, and possibly due to the interpenetrating network structure formed, depending on the concentration of the monomer.

5

The monomer(s) should preferably be dissolvable or dispersable in the solvent at the exposing step. In one embodiment the one or more monomers are dissolvable in the solvent, when the solvent is in liquid state, in gas state or in supercritical state. Preferably the one or more monomers are 10 dissolvable in the solvent its liquid and/or supercritical state.

15 The monomers may in principle be any type of polymerizable monomers. Even relatively large monomers can be used, provided that they are dissolvable or dispersable in the solvent. Since the solvent has a low surface tension is capable of dissolving a large number of different types of monomers, also monomers that are difficult to dissolve in solvents used in prior art methods.

20 In one embodiment the one or more monomers comprise at least 1 % by weight, such as at least 10 % by weight, such as at least 50 % by one or more of the monomers selected from the group consisting of silicon containing monomers such as silanes, such as TEOS (tetraethylorthosilicate or tetraethoxysilane) or chloro- or alkoxy-functional silanes, olefins such as ethylene, propylene, styrene, vinylpyrrolidone, oxygen- and nitrogen- 25 containing monomers such as acrylic derivatives, e.g. acrylic ester and acrylic acid, methacrylic acid and -ester, urethanes, mono- and di-functional alcohols, carboxylic acids, amines, isocyanates, epoxides, aromatic compounds such as aromatics carrying substituents such as alkyl groups and sulfonated aromatics, aromatic resins, imidazol and imidazol 30 derivatives, pyrazoles, quaternary ammonium compounds, polyurethane prepolymers and epoxy resins.

In one embodiment it is preferred that the one or more monomers comprise at least 50 % by weight of vinylpyrrolidone.

35

In one embodiment it is preferred that the one or more monomers comprise at least 50 % by weight of olefins.

- 5 In one embodiment it is preferred that the one or more monomers comprise at least 50 % by weight of silanes.

- 10 For providing a simple polymerization step it is in one embodiment desired that the one or more monomers are free radical polymerizable. In another embodiment the one or more monomers are polymerizable using irradiation e.g. using infrared radiation.

- 15 with a wavelength measured in vacuum of between 0.5 µm and 20 cm, such as between 0.8 µm and 10 cm, such as between 1.0 µm and 1 cm. In one embodiment the cross-linking is activated by exposing the extruded polymer to electromagnetic waves with a wavelength measured in vacuum of between 2.0 µm and 1000 µm.

- 20 Together with the monomer and optionally radical starter, other additives such as pigments and proton-conducting components may be loaded into the silicone polymer composition.

These optionally additives as well as optional radical starters may be loaded together with the monomer or they may be loaded separately.

- 25 The solvent and the exposing conditions should be selected such that the solvent has a surface tension at the exposing step of about 15 mN/m or less, such as about 10 mN/m or less, such as about 8 mN/m or less, such as about 6 mN/m or less, such as about 5 mN/m or less, such as about 0 mN/m.
- 30 Irrespectively of the state of the solvent during the exposing step, it is in one embodiment desired that the solvent has a surface tension in liquid form of about 15 mN/m or less, such as about 10 mN/m or less, such as about 8 mN/m or less, such as about 6 mN/m or less, such as about 5 mN/m or less. Thereby the monomers may be dissolved in the solvent in its liquid step prior to the exposing step.
- 35

The solvent may at the exposing step be in any of its states gas state, liquid state and supercritical state.

- 5 In one embodiment the solvent is one or more hydrocarbons or carbon-containing compounds or a composition comprising hydrocarbons or carbon-containing compounds with a Hildebrand solubility of below 11, preferably 8 or less. In this embodiment the silicone polymer composition may preferably being exposed to the solvent in its supercritical state or near it supercritical state, where the term 'near its supercritical state' means that the total pressure is at least 10 bar.
- 10

In one embodiment the solvent comprises one or more compounds from the group of C₁-C₁₂ hydrocarbons or carbon-containing compounds, preferably C₁-C₄ hydrocarbons, more preferably selected from the group consisting of methane, ethane, propane, propene, isobutane, butane, butene, isobutene, methanol, and acetone.

In one desired embodiment the solvent comprises one or both of the compounds N₂O and CO₂. The most preferred solvent is a solvent comprising CO₂.

In one embodiment the solvent comprises at least 50 %, such as at least 75%, such as at least 90% by weight of one or more of the components selected from the group consisting of CO₂, and N₂O, and C₁-C₅ hydrocarbons, the solvent preferably comprising at least 50 %, such as at least 90% of CO₂.

The solvent may also comprise a surfactant for reducing surface tension. In one embodiment the solvent comprises a surfactant preferably selected from the group of anionic, cationic, non-ionic and amphoteric surfactants, said solvent preferably comprising up to 5% by weight, such as between 0.001-50 grams of surfactant per kg solvent.

- For polymerizing and optionally crosslinking the monomer(s) it is in one embodiment desired that a radical starter in an amount preferably being sufficient to initiate the polymerization, is incorporated into the silicone polymer composition. This may be done prior to the vulcanization of the
- 5 silicone polymer composition, or after the vulcanization e.g. simultaneously with the loading of the monomer(s) into the silicone polymer composition.
- In one embodiment a radical starter is incorporated into the silicon polymer by physical compounding e.g. prior to vulcanization thereof.
- 10
- In one embodiment a radical starter is incorporated into the silicon polymer by swelling or impregnation in dissolved condition, or by co-impregnation with the one or more monomers.
- 15 In one embodiment one or more monomers are dissolved in the solvent together with a radical starter, and thereafter the solvent are swelled by the silicone polymer composition.
- The amount of radical starter could e.g. be at least 0.01 mol % of the monomer, such as at least 0.01 mol % of the monomer, such as at least 0.1 mol % of the monomer, such as at least 0.5 mol % of the monomer, such as at least 1 mol % of the monomer, such as between 1 and 10 mol % of the monomer. The skilled person will for a specific combination of monomer(s) and radical starter be able to find a suitable amount of radical starter.
- 20
- 25 The radical starter may be any kind of radical starter e.g. heat- or radiation activatable radical starters as it is known in the art. Suitable radical starters are e.g. peroxides such as dicumylperoxide or azo-compounds such as azo-bis-iso-butyronitril, or photo-labile compounds such as benzoyl-based radical starters, said radical starter preferably being.
- 30
- As mentioned the silicone polymer composition may be exposed to the solvent while the solvent is in liquid state, in gas state and/or in supercritical state. The solvent may change state during the exposing step, e.g. by changing pressure and/or temperature. As it is most simple and fast to
- 35

control the pressure, change of stated during the exposing state are most often induced by adjusting the pressure.

- In one embodiment the silicon polymer composition is exposed to the solvent
- 5 under conditions where the solvent is in a first state, followed by a change of conditions whereby the solvent changes to a second state, where the first state preferably is liquid state or supercritical state and the second state preferably is gas state.
 - 10 In one embodiment the monomer is dissolved in gas solvent, and the silicone polymer composition is exposed to the solvent while the solvent is in liquid state, in gas state and/or in supercritical state.
 - 15 In one embodiment the monomer is dissolved in supercritical solvent, and the silicone polymer composition is exposed to the solvent while the solvent is in liquid state, in gas state and/or in supercritical state.
 - 20 The amount of solvent swelled by the silicone polymer composition may vary largely, and is highly dependant on the silicone polymer composition and its vulcanization degree. Even if only small amounts are swelled the solvent may transport sufficient monomers into the silicone polymer composition as the solvents may be mobile within the silicone polymer composition and pass in and out a number of times during the exposing step.
 - 25 The exposing time may also vary in dependence on the desired amount of monomers to be loaded into the silicone polymer composition.
 - 30 In one embodiment the silicon polymer composition is exposed to said solvent for a sufficient time to swell the silicone polymer composition with the solvent, preferably to swell the silicone polymer composition with at least 0.01 %, such as at least 0.1 %, such as at least 1% by weight of solvent calculated on the weight of the silicone polymer composition.

In order to precipitate (load) as much as possible of the monomer(s) into the silicone polymer composition as fast as possible, the pressure and/or the temperature may during the exposing step be varied.

5 In one embodiment wherein the silicon polymer composition is exposed to the solvent under varying pressure, the pressure preferably may be decreased after at least a part of the solvent has been swelled into the silicone polymer composition whereby monomer(s) precipitate within the silicone composition.

10

In one embodiment wherein the silicon polymer composition is exposed to the solvent under varying temperature, the temperature preferably being decreased after at least part of the solvent has been swelled into the silicone polymer composition whereby monomer(s) precipitate within the silicone
15 composition.

In one embodiment the one or more monomers for a sufficient time to precipitate at least 0.01 %, such as at least 0.1 %, such as at least 1 % by, such as up to about 50 % by weight of monomer(s) of the total weight of the
20 silicon polymer composition.

The silicone polymer composition may in one embodiment be subjected to two or more exposing steps e.g. for increasing the amount of monomers loaded into the silicone polymer composition or to loading different
25 monomers or other additives into the silicone polymer composition in a specified order.

In one embodiment the silicone polymer composition is exposed in two or more steps to the solvent with one or more monomers to provide at total
30 monomer precipitation of at least 0.01 %, such as at least 0.1 %, such as at least 1 % by, such as up to about 50 % by weight of monomer(s) of the total weight of the silicon polymer composition. The two or more steps may be equal to each other or they may be different from each other e.g. with respect to solvent, monomer amounts and/or exposing time.

Typical exposing time for the silicon polymer composition in total is normally within 20 min, such as at least 1 min, such as for 5 min. However, the invention does not exclude higher exposing times, such as exposing times up to several hours.

5

In one embodiment it is desired that the solvent during at least a part of the exposing time is in its supercritical state.

10

In one embodiment the silicone polymer composition is subjected to an extraction step for extraction of silicon oil residues e.g. as disclosed in the co pending application PCT/DK/0300052 which is hereby incorporated by reference.

15

In one embodiment the extraction solvent used in the extraction step is identical to the solvent used in the exposing step.

20

In one embodiment the silicone polymer composition is treated with the solvent in or near its supercritical state for extracting residues followed by feeding of the monomer into the reaction chamber where the monomer is dissolved in the solvent in or near its supercritical state while the silicone polymer composition simultaneously is exposed to the solvent.

25

In one embodiment the silicone polymer composition is exposed to a solvent consisting essentially of carbon dioxide. The CO₂ is carrying the monomer(s) in or near its supercritical state, for a sufficient time to swell the silicone polymer composition with the solvent containing the monomer(s).

30

The silicone polymer composition may preferably prior to the exposing step be shaped to the desired shape, e.g. using extrusion, injecting-moulding, calendering, pressing or cutting as it is well known in the art.

35

The IPNs produced using the method as disclosed above are useful as engineering materials for automotive switches and displays, telecom applications such as EMI shielding, gas separation membranes, membranes for fuel cells and carriers for heterogeneous catalysts.

The IPN produced according to the invention may further be suitable as general light spreading medium, e.g. as lamp cover.

- 5 The invention also relates to a method of producing a polymeric unit in particular suitable for automotive or telecom use. This method comprise the steps of producing an IPN as described above followed by a surface treatment e.g. by plasma or flame surface activation and subsequent painting, or immediate painting or coating.
 - 10 The silicone polymer composition used for the IPN for automotive or telecom use may preferably be transparent. When using a transparent silicone polymer composition the resulting product may as described above be of milky-white appearance, presumably due to a microstructure of small domains in size below or in the order of the wavelength of visible light, in addition due to different refractive indices of silicone versus monomer, and possibly due to the interpenetrating network structure formed, depending on the concentration of the monomer.
 - 15 Such a resulting milky-white appearance is preferred for switches illuminated from the backside due to even spreading of light. Furthermore, danger of destroying the thin white paint layer by laser cutting or similar is reduced due to the thickness of the milky-white layer.
 - 20 In this connection it should be observed that prior art silicone parts are used, e.g. as covers for switches such as steering wheel switches. Such prior art silicone parts are normally produced from transparent silicone applied with a thin white paint layer as well as a darker paint layer which is applied after a suitable surface activation process, e.g. plasma or flame treatment. Symbols
 - 25 are being cut through the dark paint layer using a laser. This way, the switch symbols can be illuminated from the inner side of the switch. Both surface activation and application of a thin paint layer of controlled thickness are however, difficult, expensive and labor-intensive.

Using the method of the present invention, one painting step is avoided in typical white-plus-colour combinations designed for subsequent laser cutting of symbols.

- 5 In one embodiment, the impregnated reactive monomer is made adhesive to paint, e.g. by using styrene, acrylics, urethanes which can chemically add to reactive parts of the paint formulation. This way, plasma or other surface treatment prior to painting is avoided. This way, a cheap and technically improved route is opened.

10

The invention also relates to a method of producing a polymer membrane comprising the steps of:

- 15 -producing an IPN unit shaped as a membrane according to the disclosure above, wherein the membrane has a thickness between 5 and 1000 µm.

The amount of monomer precipitated into the membrane shaped silicone polymer composition is preferably 5 % by weight or less, such as 2% or less or such as 1% and less.

20

The membrane may preferably be a membrane for separation of gases or liquids.

- 25 In one embodiment the membrane is a fuel cell membrane. The membrane preferably being less permeable to gases than the original silicone composition at least by a factor of 2. Furthermore it is preferred that the conductivity for protons (H^+) preferably is increased in comparison with the original silicone composition by incorporation of proton-conducting monomers such as imidazol or imidazol derivatives. The conductivity for 30 protons (H^+) preferably being increased in comparison with the original silicone composition by a factor of at least 10, such as at least 100.

- 35 A membranes for fuel cells obtained according to the present invention is relatively cheap, oxidation stable and has low tendencies to dry out compared to prior art fuel cell membranes.

Silicone is highly oxidation stable. In advanced applications, fluorinated silicones or silicones carrying phenyl groups may preferably be used.

Reactive monomers are chosen which preferably carry as little as possible

- 5 tertiary H-atoms which are particularly prone to oxidation.

Furthermore using the present invention it is possible in a simple manner to produce a membrane that is selectively permeable (or conductive) for protons respectively hydroxide ions.

10

The danger of drying out (loss of water) does practically not exist in case imidazol derivatives or other proton carriers are used.

15

The invention also relates to the IPN obtained using the methods as disclosed above

The IPN is preferably a full IPN comprising at least two interpenetrating, individually cross linked networks.

20

Since the IPN can be produced in the absence of organic solvents the IPN may preferably be free of organic solvents. Even though organic solvents may be used in the production, the use of solvent comprising CO₂ which is preferred result in an essentially organic solvent free product.

25

The IPN may in one embodiment comprise a network of a polymer selected from the group consisting of polyvinylpyrrolidone.

30

EXAMPLES

Automotive parts:

- A transparent silicone rubber is exposed to pressurized carbon dioxide which is able to extract volatile or low molecular weight residues from the rubber. At the same time (or later), a reactive monomer such as silanes such as TEOS, styrene, acrylic derivatives (such as acid or ester), vinylpyrrolidone,
- 5 isocyanate or any other reactive monomer is introduced, dissolved in carbon dioxide. Optionally, a radical starter such as azo-bis-iso-butyronitrile, peroxides or the like is added in small concentrations such as 1% of the reactive monomer. The reactive monomer is evenly distributed within the silicone rubber, such as at 4% wt. of the rubber. Following removal of the
- 10 solvent carbon dioxide, residual monomer can be recycled or discarded.
- The polymer products are exposed to high temperature, e.g. in the same reactor which is used for carbon dioxide treatment, to let the reactive monomer polymerize.
- 15 The resulting product is of milky-white appearance, presumably due to a microstructure of small domains in size below or in the order of the wavelength of visible light, in addition due to different refractive indices of silicone versus monomer, and possibly due to the interpenetrating network structure formed, depending on the concentration of the monomer.
- 20
- Membranes for fuel cells:*
- Manufacturing as described under automotive. The target membrane is not permeable for gases, but conductive for protons or hydroxide ions. In
- 25 addition, good contact to porous, e.g. ceramic electrodes is desired.
- Useful monomers are silanes such as TEOS, styrene, aromatic compounds carrying groups which render the molecule less mobile and volatile, such as trialkyl-groups, optionally the aromatic core(s) being sulfonated or otherwise
- 30 converted into acids, aromatic resins, typical known proton carriers such as imidazol derivatives, pyrazoles, quaternary ammonium compounds and various others.

The loading of silicone rubber with reactive monomer may be carried out more than once in order to achieve maximum loading, i.e. limited gas permeability:

5

Gas separation membranes:

A low degree of loading of reactive monomers, such as 0.1% weight of silicone, is chosen to modify thin tubes of silicone rubber. This way, the high
10 gas permeability of silicone is preserved, however, the reactive monomer modifies the permeability of certain gases. Paraffinic impregnation, as one example, hinders the diffusion of paraffinic gases and allows the separation, e.g. of methane and oxygen.

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CLAIMS

1. A method of producing an interpenetrating polymer network (IPN)
5 comprising the steps of
 - i) providing a silicone polymer composition,
 - ii) providing one or more monomers for a polymer,
10
 - iii) providing a solvent for the one or more monomers,
 - iv) exposing said silicone polymer composition to said one or more monomer
and said solvent to precipitate monomer within said silicone polymer
15 composition
 - v) polymerizing said monomer to form an IPN,
wherein said solvent has a surface tension at the exposing step of about
15 mN/m or less, such as about 10 mN/m or less, such as about 8 mN/m or
20 less, such as about 6 mN/m or less, such as about 5 mN/m or less, such as
about 0 mN/m.
2. A method of producing an IPN according to claim 1 wherein said
25 solvent has a surface tension in liquid form of about 15 mN/m or less, such
as about 10 mN/m or less, such as about 8 mN/m or less, such as about 6
mN/m or less, such as about 5 mN/m or less.
3. A method of producing an IPN according to any one of the claims 1 and
30 2 wherein said silicone polymer composition comprises at least 10 %, such
as at least 20%, such as at least 40%, such as at least 60 % by weight of
polymer having a backbone consisting of Si and O molecules.
4. A method of producing an IPN according to any one of the claims 1 and
35 2 wherein said silicone polymer composition comprises at least 10 %, such

as at least 20%, such as at least 40%, such as at least 60 % by weight of polymer having a backbone consisting of Si molecules.

5. A method of producing an IPN according to any one of the preceding claims wherein said silicone polymer composition comprises at least 10 %, such as at least 20%, such as at least 40%, such as at least 60 % by weight of polysiloxane polymer.
10. 6. A method of producing an IPN according to any one of the preceding claims wherein said silicone polymer composition comprises one or more polymers selected from the group consisting of dimethyl polysiloxan, methylphenyl polysiloxane, fluorosilicone rubber, silicone esters, polysiloxanes, polysilanes, chlorosilanes, alkoxy silanes, aminosilanes, polysilanes polydialkylsiloxanes, polysiloxanes containing phenyl substituents, said polymers of the silicone polymer composition optionally being vinyl-functionalized and/or optionally being partially or fully fluorinated.
20. 7. A method of producing an IPN according to any one of the preceding claims wherein said silicone polymer composition comprises up to 90 % by weight of non-silicone polymers or co-polymers, fillers and/or additives, said non-silicone polymers e.g. being thermoplastics or thermosets, preferably selected from the group consisting of polyolefins, polyesters, polyurethanes, polycarbonates, polyvinyl polymers, said fillers e.g. being particles or fibres e.g. in the form of minerals or organic fillers, preferably selected from the 25 group consisting of silica, metals, metal oxides, mixed metal oxides, glass beads or glass fibers, and said additives e.g. being selected from the group consisting of adhesion promoters for 2K-constructions, process and plasticizing oils, antioxidants and pigments.
30. 8. A method of producing an IPN according to any one of the preceding claims wherein said silicone polymer composition is partially vulcanized, such as up to a vulcanization degree (cross-linking degree) of at least 50%, such as at least 70%, such as at least 90% or wholly, such as at least 96%, such as at least 97%, such as at least 98%.

9. A method of producing an IPN according to any one of the preceding claims wherein said silicone polymer composition is a vulcanized rubber.
10. A method of producing an IPN according to any one of the preceding 5 claims wherein said one or more monomers are dissolvable in said solvent, when said solvent is in liquid state, in gas state or in supercritical state, said monomer preferable being dissolvable in the solvent its liquid and/or supercritical state.
11. A method of producing an IPN according to any one of the preceding 10 claims wherein said one or more monomers comprise at least 1 % by weight, such as at least 10 % by weight, such as at least 50 % by one or more of the monomers selected from the group consisting of silicon containing monomers such as silanes, such as TEOS (tetraethylorthosilicate or 15 tetraethoxysilane) or chloro- or alkoxy-functional silanes, olefins such as ethylene, propylene, styrene, vinylpyrrolidone, oxygen- and nitrogen-containing monomers such as acrylic derivatives, e.g. acrylic ester and acrylic acid, methacrylic acid and -ester, urethanes, mono- and di-functional alcohols, carboxylic acids, amines, isocyanates, epoxides, aromatic 20 compounds such as aromatics carrying substituents such as alkyl groups and sulfonated aromatics, aromatic resins, imidazol and imidazol derivatives, pyrazoles, quarternary ammonium compounds, polyurethane prepolymers and epoxy resins.,
12. A method of producing an IPN according to any one of the preceding 25 claims 1-10 wherein said one or more monomers comprise at least 50 % by weight of vinylpyrrolidone.
13. A method of producing an IPN according to any one of the preceding 30 claims 1-10 wherein said one or more monomers comprise at least 50 % by weight of olefins.
14. A method of producing an IPN according to any one of the preceding 35 claims 1-10 wherein said one or more monomers comprise at least 50 % by weight of silanes.

15. A method of producing an IPN according to any one of the preceding claims wherein said one or more monomers are free radical polymerizable.
- 5 16. A method of producing an IPN according to any one of the preceding claims wherein the solvent is one or more hydrocarbons or carbon-containing compounds or a composition comprising hydrocarbons or carbon-containing compounds with a Hildebrand solubility of below 11, preferably 8 or less, the silicone polymer composition preferably being exposed to the solvent in its 10 supercritical state or near it supercritical state, where the term 'near its supercritical state' means that the total pressure is at least 10 bar.
- 15 17. A method of producing an IPN according to any one of the preceding claims wherein the solvent comprises one or more compounds from the group of C₁-C₁₂ hydrocarbons or carbon-containing compounds, preferably C₁-C₄ hydrocarbons, more preferably selected from the group consisting of methane, ethane, propane, propene, isobutane, butane, butene, isobutene, methanol, acetone, N₂O and CO₂, more preferably the solvent comprises CO₂, the silicone polymer composition being exposed to the solvent in 20 supercritical state.
- 25 18. A method of producing an IPN according to any one of the preceding claims wherein the solvent has a surface tension in liquid form of about 15 mN/m or less, such as about 10 mN/m or less, such as about 8 mN/m or less, such as about 6 mN/m or less, such as about 5 mN/m or less, the silicone polymer composition being exposed to the solvent while it is in one or more of its states liquid state, gas state and supercritical state.
- 30 19. A method of producing an IPN according to claim 18 wherein said solvent comprises at least 50 %, such as at least 75%, such as at least 90% by weight of one or more of the components selected from the group consisting of CO₂, and N₂O, and C₁-C₅ hydrocarbons, the solvent preferably comprising at least 50 %, such as at least 90% of CO₂.

20. A method of producing an IPN according to any one of the preceding claims wherein the solvent comprises a surfactant preferably selected from the group of anionic, cationic, non-ionic and amphoteric surfactants, said solvent preferably comprising up to 5% by weight, such as between 0.001-50
5 grams of surfactant per kg solvent.
21. A method of producing an IPN according to any one of the preceding claims wherein a radical starter is incorporated into said silicon polymer, preferably by physical compounding, by swelling or impregnation in dissolved
10 condition, or by co-impregnation with the one or more monomers, the amount of radical starter preferably being sufficient to initiate the polymerization.
22. A method of producing an IPN according to any one of the preceding
15 claims wherein said one or more monomers are dissolved in the solvent together with a radical starter, the amount of radical starter preferably being sufficient to initiate the polymerization.
23. A method of producing an IPN according to any one of the claims 21
20 and 22 wherein the amount of radical starter is at least 0.01 mol % of the monomer, such as at least 0.01 mol % of the monomer, such as at least 0.1 mol % of the monomer, such as at least 0.5 mol % of the monomer, such as at least 1 mol % of the monomer, such as between 1 and 10 mol % of the monomer.
25
24. A method of producing an IPN according to any one of the preceding claims 21-23 wherein said radical starter is selected from the group consisting of peroxides such as dicumylperoxide or azo-compounds such as azo-bis-iso-butyronitril, or photo-labile compounds such as benzoyl-based
30 radical starters, said radical starter preferably being heat- or radiation activatable.
25. A method of producing an IPN according to any one of the preceding claims wherein said monomer is dissolved in liquid solvent, said silicone

polymer composition being exposed to said solvent while the solvent is in liquid state, in gas state and/or in supercritical state.

26. A method of producing an IPN according to any one of the preceding
5 claims 1-24 wherein said monomer is dissolved in gas solvent, said silicone polymer composition being exposed to said solvent while the solvent is in liquid state, in gas state and/or in supercritical state.

27. A method of producing an IPN according to any one of the preceding
10 claims 1-24 wherein said monomer is dissolved in supercritical solvent, said silicone polymer composition being exposed to said solvent while the solvent is in liquid state, in gas state and/or in supercritical state.

28. A method of producing an IPN according to any one of the preceding
15 claims wherein said silicon polymer composition is exposed to said solvent for a sufficient time to swell the silicone polymer composition with the solvent, preferably to swell the silicone polymer composition with at least 0.01 %, such as at least 0.1 %, such as at least 1% by weight of solvent calculated on the weight of the silicone polymer composition.
20

29. A method of producing an IPN according to any one of the preceding claims wherein said silicon polymer composition is exposed to said solvent under varying pressure, the pressure preferably being decreased after at least a part of the solvent has been swelled into the silicone polymer
25 composition whereby monomer(s) precipitate within the silicone composition.

30. A method of producing an IPN according to any one of the preceding claims wherein said silicon polymer composition is exposed to said solvent under varying temperature, the temperature preferably being decreased after
30 at least part of the solvent has been swelled into the silicone polymer composition whereby monomer(s) precipitate within the silicone composition.

31. A method of producing an IPN according to any one of the preceding claims wherein said silicon polymer composition is exposed to said solvent
35 under conditions where the solvent is in a first state, followed by a change of

conditions whereby the solvent changes to a second state, said first state preferably being liquid state or supercritical state and said second state preferably being gas state.

- 5 32. A method of producing an IPN according to any one of the preceding claims wherein said silicon polymer composition is exposed to said solvent with said one or more monomers for a sufficient time to precipitate at least 0.01 %, such as at least 0.1 %, such as at least 1 % by, such as up to about 50 % by weight of monomer(s) of the total weight of the silicon polymer 10 composition.
- 15 33. A method of producing an IPN according to any one of the preceding claims wherein said silicon polymer composition is exposed in two or more steps to said solvent with one or more monomers to provide at total monomer precipitation of at least 0.01 %, such as at least 0.1 %, such as at least 1 % by, such as up to about 50 % by weight of monomer(s) of the total weight of the silicon polymer composition, said two or more steps being equal or different from each other e.g. with respect to solvent, monomer amounts and/or exposing time.
- 20 34. A method of producing an IPN according to any one of the preceding claims 31 and 32 wherein said silicon polymer composition is exposed to said solvent with said one or more monomers for a total time of at least 1 min, such as for 5 min, such as for 20 min or more.
- 25 35. A method of producing an IPN according to any one of the preceding claims 1-16 wherein said silicone polymer composition is treated with the solvent in or near its supercritical state (for extracting residues) followed by feeding of the monomer into the reaction chamber where the monomer is dissolved in the solvent in or near its supercritical state while the silicone polymer composition simultaneously is exposed to the solvent.
- 30 36. A method of producing an IPN according to any one of the preceding claims wherein said silicone polymer composition is exposed to a solvent consisting essentially of carbon dioxide and carrying the monomer(s) in or

near its supercritical state, for a sufficient time to swell the silicone polymer composition with the solvent with monomer(s).

37. A method of producing an IPN according to any one of the preceding
5 claims wherein said silicone polymer composition prior to the exposing step
is shaped, preferably by extrusion, injecting-moulding, calendaring, pressing
or cutting.

38. A method of producing a polymeric unit (for automotive or telecom use)
10 comprising the steps of:

-producing an IPN unit in the desired shape according to any one of the
preceding claims 1-37, and

15 -treating the surface thereof, e.g. by plasma or flame surface activation and
subsequent painting, or immediate painting or coating.

39. A method of producing a polymeric unit according to claim 38 wherein
the silicone polymer composition used for the IPN is transparent.

20 40. A method of producing a polymer unit according to any one of the
claims 38 and 39 wherein the one or more monomers comprise one or more
from the group of styrene, acrylics and urethanes

25 41. A method of producing a polymer membrane comprising the steps of:

-producing an IPN unit shaped as a membrane according to any one of the
preceding claims 1-37, wherein the membrane has a thickness between 5
and 1000 µm.

30 42. A method of producing a polymer membrane according to claim 41
wherein the amount of monomer precipitated into the silicone polymer
composition is 5 % by weight or less, such as 2% or less or such as 1% and
less.

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43. A method of producing a polymer membrane according to any one of the claims 41 and 42 wherein the membrane is a membrane for separation of gases or liquids.
- 5 44. A method of producing a polymer membrane according to any one of the claims 41 and 42 wherein the membrane is a fuel cell membrane, said membrane preferably being less permeable to gases than the original silicone composition at least by a factor of 2, and whereby the conductivity for protons (H⁺) preferably is increased in comparison with the original
10 silicone composition by incorporation of proton-conducting monomers such as imidazol or imidazol derivatives, the conductivity for protons (H⁺) preferably being increased in comparison with the original silicone composition by a factor of at least 10, such as at least 100.
- 15 45. An IPN obtainable according to any one of the preceding claims 1-37.
46. An IPN according to claim 45 wherein the IPN is a full IPN comprising at least two interpenetrating, individually cross linked networks.
- 20 47. An IPN according to any one of the preceding claims 45 and 46 wherein the IPN is essentially free of organic solvents.
- 25 48. An IPN according to any one of the preceding claims 45-47 wherein the IPN comprises a network of a polymer selected from the group consisting of polyvinylpyrrolidone.
49. An automotive part obtainable according to any one of the claims 38-40.
50. A telecom part obtainable according to any one of the claims 38-40.
30
51. A medical device such as catheter, part of a pace maker and an implant.
52. A gas separation membrane obtainable according to any one of the claims 41-43.
35

53. A fuel cell membrane obtainable according to any one of the claims 41, 42 and 44.

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